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HEXABROMOAZOBENZENE AND HEXABROMOHYDROBENZENE

A THESIS
SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL
OF THE UNIVERSITY OF MINNESOTA

BY

CARYL SLY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
SEPTEMBER 1927

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[Reprint from the Journal of the American Chemical Society, 54, 3348 (1932).]

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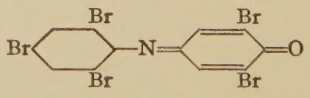
THE OXIDATION OF SYMMETRICAL TRIBROMOANILINE BY CHROMIC ANHYDRIDE IN ACID SOLUTION. II. MECHANISM[1]

By W. H. Hunter and Caryl Sly

Received April 11, 1932 Published August 5, 1932

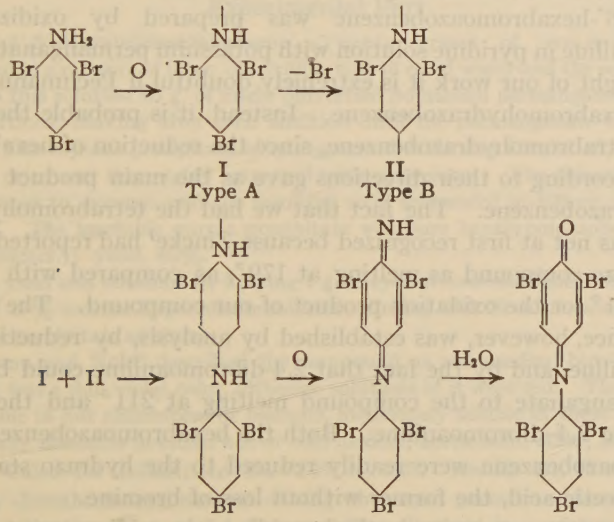
In some unpublished work performed in this Laboratory by A. G. Mayers (now deceased), it was found that symmetrical tribromoaniline, dissolved in a mixture of acetic and dilute sulfuric acids, on oxidation with chromic anhydride gave a compound with the molecular formula $C_{12}H_4ONBr$, and the structural formula



[1] Abstracted from a thesis submitted by Caryl Sly to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, August, 1927. The manuscript was written by the junior author after the death of Dr. Hunter.—L. I. Smith.

Brominated N-phenylquinoneimines have been prepared by Smith and Orton[2] by first brominating *p*-hydroxydiphenylamine and then oxidizing with chromic anhydride. However, no reference could be found relative to the formation of such compounds by the oxidation of halogenated anilines.

Consideration of the probable mechanism for the formation of the above compound by oxidation of symmetrical tribromoaniline led to two widely divergent views of the reaction. Goldschmidt[3] has shown in the oxidation of anilines that a radical of the type C_6H_5NH— is first formed, which may react as such or be further oxidized to the type $C_6H_5N<$. This latter radical in his opinion was responsible for the formation of azobenzene and quinone diimine by the oxidation of aniline. The radical C_6H_5NH— is the nitrogen analog of the type A radicals which result during the oxidation of *sym.*-trihalogenated phenols.[4] Using the type A and type B radicals predicated in the case of the halogenated phenols the reaction becomes



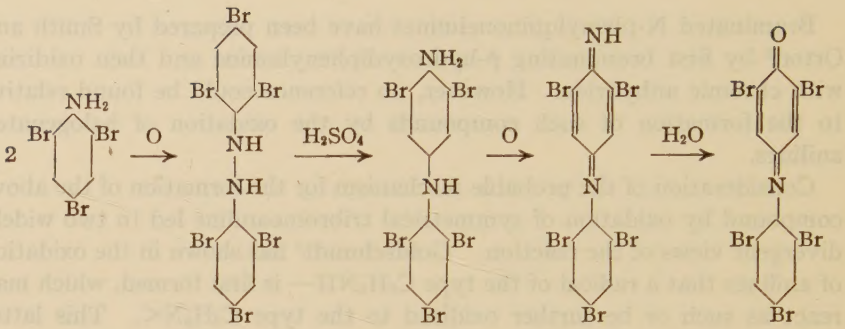
The alternative mechanism assumed the formation of *sym.*-hexabromohydrazobenzene, a *p*-semidine rearrangement of this derivative with the loss of a bromine atom, oxidation to the quinonediimine and finally hydrolysis to the quinoneimine.

In order to choose between these mechanisms an attempt was made to prepare the pentabromoquinoneimine from *sym.*-hexabromohydrazobenzene. The preparation of hexabromohydrazobenzene presented consider-

[2] Smith and Orton, *J. Chem. Soc.*, **93**, 314–326 (1908).

[3] Goldschmidt, *Ber.*, **55**, 3216 (1922).

[4] Hunter and Levine, THIS JOURNAL, **48**, 1608 (1926); Hunter and Morse, *ibid.*, **48**, 1615 (1926).



able difficulty despite the fact that it had been previously reported by Pechmann and Nold.[5]

Production of the desired hydrazo derivative from *sym.*-tribromonitrobenzene was not successful because at least one bromine was lost in alkaline reduction, a condition already observed by other workers.[6] Eventually 2,4,6,2′,4′,6′-hexabromoazobenzene was prepared by oxidizing *sym.*-tribromoaniline in pyridine solution with potassium permanganate.

In the light of our work it is extremely doubtful if Pechmann and Nold had the hexabromohydrazobenzene. Instead, it is probable they had the 2,4,2′,4′-tetrabromohydrazobenzene, since the reduction of hexabromoazobenzene according to their directions gave as the main product this tetrabromohydrazobenzene. The fact that we had the tetrabromohydrazo derivative was not at first recognized because Zincke[7] had reported the corresponding azo compound as melting at 179°, as compared with a melting point of 211° for the oxidation product of our compound. The identity of the substance, however, was established by analysis, by reduction to 2,4-dibromoaniline, and by the fact that 2,4-dibromoaniline could be oxidized with permanganate to the compound melting at 211° and then reduced back to the 2,4–dibromoaniline. Both the hexabromoazobenzene and the tetrabromoazobenzene were readily reduced to the hydrazo state by zinc dust and acetic acid, the former without loss of bromine.

All of our attempts to cause the benzidine or semidine rearrangement of the hexabromoazobenzene or hexabromohydrazobenzene met with failure. Using the azo derivative, Jacobson's method[8] or Witt's method[9] gave only reduction products. With the hydrazo derivative, concentrated hydrochloric acid or 65% sulfuric acid[10] caused only oxidation and reduction to

[5] Pechmann and Nold, *Ber.*, **31**, 564 (1898).

[6] Jackson and Bentley, *Am. Chem. J.*, **14**, 364 (1892).

[7] Zincke and Kuchenbecker, *Ann.*, **330**, 54 (1904).

[8] Jacobson, *Ann.*, **287**, 105, 110, 128 (1895).

[9] Witt, *Ber.*, **27**, 2382 (1894).

[10] Meyer, *Ber.*, **53**, 2035, 2045 (1920), reports that sulfuric acid caused rearrangement in a similar case where hydrochloric acid failed.

the azo compound and the substituted aniline. Tauber's method[11] of treating the hydrazo compound with a reducing agent and a mineral acid gave only reduction to the aniline. Similar results were obtained in the case of the tetrabromoazobenzene and tetrabromohydrazobenzene. The usual tests[12] for *o*- and *p*-semidine rearrangement products were negative.

As a final test for the formation of pentabromoquinoneimine from *sym.*-hexabromohydrazobenzene, the hydrazo compound was added to the reaction mixture which had oxidized *sym.*-tribromoaniline to the pentabromoquinoneimine. Here the only reaction was one of oxidation to hexabromoazobenzene.

In view of these results it seems probable that the oxidation of *sym.*-tribromoaniline in acid solution with chromic anhydride involves the same reaction mechanism as that previously postulated for the oxidation of symmetrically halogenated phenols, with the intermediate formation of the N analogs of the type A and type B radicals.

Experimental Part

2,4,6,2′,4′,6′-Hexabromoazobenzene.—Twenty grams of *sym.*-tribromoaniline was dissolved in a mixture of 90 cc. of pyridine and 46 cc. of water and the solution heated to 75°. To this solution 40 g. of finely pulverized potassium permanganate was added in small portions, shaking after each addition until the permanganate color had disappeared. The copious precipitate of manganese dioxide was filtered off, washed with cold water, dried and thoroughly extracted with chloroform. The chloroform solution was evaporated to dryness, and the resulting solid suspended in 100 cc. of acetic acid held at 80°. The insoluble purple precipitate was pure hexabromoazobenzene, m. p. 212–213° (uncorr.); yield, 40%.

A 20% yield was obtained by heating 1 g. of *sym.*-tribromoaniline, 5 cc. of pyridine and 1 cc. of 17% sodium hypochlorite solution, diluting with 50 cc. of water and treating the insoluble precipitate as above.

Pechmann and Nold[5] described the compound as red needles, but in every case our product was a dull violet color, although solutions of it were red. The substance is readily soluble in hot chloroform or benzene, moderately soluble in these solvents cold and practically insoluble in either hot or cold alcohol, acetic acid, ether, and acetone.

Anal. Calcd. for $C_{12}H_4N_2Br_6$: Br, 73.17, N, 4.27. Found: Br, 73.17; N, 4.29.

2,4,2′,4′-Tetrabromoazobenzene.—Using the same procedure described for the hexabromo derivative, 20 g. of 2,4-dibromoaniline dissolved in a mixture of 40 cc. of pyridine and 40 cc. of water was treated with 40 g. of potassium permanganate. The dried mixture of manganese dioxide and azo derivative was extracted with 200 cc. of benzene until no further coloration of the benzene resulted. On cooling the benzene solution a considerable portion of the azo compound crystallized as red needles. These were filtered off, the mother liquor evaporated to 50 cc. and 100 cc. of hot 95% alcohol added; yield, 40%; m. p. 211° (uncorr.).

Fifty to sixty per cent. yields were also obtained by reducing *sym.*-hexabromoazobenzene suspended in alcohol with zinc dust and ammonium chloride and then oxidizing the product thus formed in acetic acid with chromic anhydride.

[11] Tauber, *Ber.*, **25**, 1022 (1892).

[12] Witt and Schmidt, *ibid.*, **25**, 1017 (1892), and Ikuta, *Ann.*, **243**, 281 (1887); *Ber.*, **27**, 2707 (1894).

The substance crystallizes in red needles from benzene, is very soluble in either hot chloroform or benzene, slightly soluble in hot acetic acid and practically insoluble in alcohol.

Anal. Calcd. for $C_{12}H_6N_2Br_4$: Br, 64.26; N, 5.62. Found: Br, 63.74, 63.61; N, 5.63, 6.03.

2,4,2′,4′-Tetrabromohydrazobenzene.—Two and one-half grams of tetrabromoazobenzene dissolved in a boiling mixture of 40 cc. of benzene and 5 cc. of acetic acid was stirred vigorously with 1 to 3 g. of zinc dust, added in small portions. The excess zinc was filtered from the colorless solution and the filtrate evaporated to 5 cc. One cc. of water and 5 cc. of acetic acid were added, and the solution chilled, giving colorless needles of m. p. 123–124° (uncorr.); yield, 80%. Reduction with stannous chloride gave 2,4-dibromoaniline.

Anal. Calcd. for $C_{12}H_8N_2Br_4$: Br, 64.00; N, 5.60. Found: Br, 63.70; N, 5.99.

N,N′-Diacetyl-2,4,2′,4′-tetrabromohydrazobenzene.—One gram of tetrabromohydrazobenzene was added to 25 cc. of cold acetic anhydride and the mixture allowed to stand for two days, then heated to 40° and cooled. The azo derivative which had formed was filtered off and the excess acetic anhydride destroyed with hot water. The insoluble material after treatment with water was recrystallized from dilute alcohol as colorless crystals, m. p. 178–179°C. (uncorr.); yield, 40%.

Anal. Calcd. for $C_{16}H_{12}O_2N_2Br_4$: Br, 54.80. Found: Br, 54.22.

Rearrangement Experiments.—All of our attempts to rearrange either the hexabromohydrazobenzene or the tetrabromohydrazobenzene met with failure. Mineral acids without a reducing agent present and at elevated temperatures gave only the azo

TABLE I

REARRANGEMENT EXPERIMENTS ON HEXABROMOHYDRAZOBENZENE

Reaction of 1 g. of hexabromohydrazobenzene and	Hexabromoazobenzene, g.	*Sym.*-tribromoaniline, g.	Recovered, %
20 cc. concd. HCl, sealed tube, 130°	0.46	0.51	97
20 cc. 66% H_2SO_4, sealed tube, 150°	.43	.52	95
25 cc. abs. alcohol, 10 cc. concd. HCl, 1 g. $SnCl_4$, 80° for 12 hrs.; stood for 3 days	.40	.55[a]	95
25 cc. abs. alcohol, 10 cc. 66% H_2SO_4, 80° for 12 hrs., stood for 3 days	.42	.52[a]	94
30 cc. cold abs. alcohol, 1 g. $SnCl_2 \cdot H_2O$, 5 cc. concd. HCl, stood for 48 hrs.	.93 unchanged hydrazo	.05	98

[a] Contained small amounts of unchanged hexabromohydrazobenzene.

TABLE II

REARRANGEMENT EXPERIMENTS ON TETRABROMOHYDRAZOBENZENE

Reaction of 1 g. of tetrabromohydrazobenzene and	Tetrabromoazobenzene, g.	2,4-Dibromoaniline, g.	Recovered, %
10 cc. concd. HCl, sealed tube, 130°	0.45	0.47	92
10 cc. 66% H_2SO_4, sealed tube, 100–130°	.45	.42	87
25 cc. abs. alcohol, 10 cc. concd. HCl, 1 g. $SnCl_4$, 80° for 12 hours, stood for 3 days	.48	.40	88
25 cc. abs. alcohol, 10 cc. 66% H_2SO_4, 80° for 12 hrs., stood for 3 days	.47	.46	93
25 cc. abs. alcohol, 1 g. $SnCl_2 \cdot 2H_2O$, 5 cc. concd. HCl, stood for 48 hrs.	.85 unchanged hydrazo	.12	97

derivative and the aniline, while in the cold, stannous chloride in the presence of hydrochloric acid gave the aniline along with the unchanged hydrazobenzene.

The tables indicate the conditions of attempted rearrangement and the products isolated.

Summary

1. A study of the properties of *sym.*-hexabromohydrazobenzene has shown that it cannot be responsible for the formation of a pentabromoquinoneimine obtained by the oxidation of *sym.*-tribromoaniline in acid solution with chromic anhydride. It is, therefore, probable that N analogs of the type A and type B radicals postulated in the oxidation of *sym.*-halogenated phenols play the important role.

2. *Sym.*-hexabromohydrazobenzene and 2,4,2′,4′-tetrabromohydrazobenzene do not undergo the benzidine type of rearrangement. Instead they oxidize and reduce to the corresponding azo and aniline derivatives in the presence of a mineral acid without a reducing agent; in the presence of a reducing agent they are split to the anilines.

3. A method for the preparation of azo compounds is described.

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